

# Springtime Peaks of Trace Metals in Antarctic Snow

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Drifting snow samples were collected at Asuka Station (71°32'S, 24°08'E, 930 m above sea level) over a period from July to December 1991; 36 elements (including Na, Mg, K, Ca, Fe, Al, Li, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Se, Rb, Sr, Cd, Pb, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th) in snow were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) by direct sample introduction. Concentrations of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  in the snow were also determined by ion chromatography. In late September to early October, there was a pronounced peak concentration of most of the elements together with non-sea salt sulfate. Enrichment factor analyses suggest that Na, Mg, Ca, K, and Sr are of marine origin and Al, Fe, Mn, Rb, Cr, Ni, Ga, V, and all the rare earth elements are of crustal origins. Volcanic eruption of Mt. Pinatubo (June 1991) and Mt. Hudson (August 1991) could be the reason for the precipitation of Pb, Cd, Cu, Zn, and Se together with non-sea salt sulfates in the austral spring at Asuka Station. **Key words:** Antarctic snow,  $\text{Cl}^-$ , enrichment factor, ICP-MS,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , trace metals, volcanic eruption. *Environ Health Perspect* 105:654–659 (1997)

Because the polar regions are remote from anthropogenic pollution sources, chemical constituents of Antarctic snow reflect the background level of the pollution in the atmosphere (1,2). Various substances are transported over the Antarctic through the atmosphere (3) and deposited onto the snow surface (4,5), but their mechanisms and possible sources are not yet fully understood. Particularly, polar stratospheric precipitation in Antarctic snow has recently attracted many investigators to the connection with the Antarctic ozone hole (6–8).

Chemical constituent concentrations in air and snow in the Arctic area show a distinct seasonal pattern caused by a variation in long-range atmospheric circulation in high and midlatitude areas (9,10). Airborne sulfate and several trace metals of crustal and anthropogenic origin show strong peaks in spring; this is known as Arctic haze (9,10). In the Antarctic, a seasonal pattern of crustal, marine, and sulfate aerosol concentration has been reported at the South Pole (11–13) and at a coastal region (14) with a maximum for the crustal and sulfate species and with a minimum for the marine component during austral summer. But there are few studies of snow in Antarctica that clarify autumn–spring peaks of Pb in the east coast of the Antarctic Peninsula (15) and summer peaks of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations at Mizuho Station (16). However, available data sets for long- and short-term changes in chemical components in Antarctic snow are still limited.

Chemical constituent concentrations in air and snow in Arctic and Antarctic areas are extremely low. Previous analyses of trace elements in polar snow have been carried

out by graphite furnace atomic absorption following a preconcentration in a clean room (1,2,4,5,14). After the introduction of inductively coupled plasma-mass spectrometry (ICP-MS), which is a well established powerful technique for the determination of trace elements, it becomes possible to determine as many as 40 elements at detection limits of below the order of parts per trillion (ppt) (17,18). The present data set, however, is probably one of the most extensive so far reported for trace elements in precipitation in the Antarctic. In this study, we present temporal variations of trace elements in the Antarctic area and discuss their using enrichment factors.

## Methods

**Field sampling.** From July to December 1991, drifting snow samples were collected at Asuka Station (71°32'S, 24°08'E, 930 m above sea level). Snow was obtained by the snow trap method reported by Osada et al. (16). Sampling was carried out with special care to avoid contamination. Asuka Station is located 120 km from the coast in Queen Maud Land, East Antarctica (Fig. 1). The Sør Rondane Mountains are situated several hundred kilometers south of the station. At the station, katabatic winds prevail with the mean wind speed of 12.6 m/sec in an east southeast direction (19). Net accumulation of snow over January to November 1991 at the station was estimated as 35 cm by the snow stake method (19); the deviation of the stake measurements was within 10 cm in the period of this study (19).

**Chemical analysis.** Snow samples were collected in specially prepared polyethylene bottles, which had been thoroughly

washed with nitric acid and distilled water. The samples were kept frozen until the analytical stage. Sample pretreatment, such as preconcentration or filtration, was not performed. Two sets of running conditions of ICP-MS (ELAN 6000, Perkin Elmer, Osaka, Japan) were used. For the analyses of Ca, Mg, K, and Al, the RF power was 1000 W and the nebulizer gas flow rate was 0.725 l/min; for all other elements, the RF power was 600 W and the nebulizer gas flow rate was 1 l/min. Sampling cones and skimmer cones were made of Pt. Ultra pure water (TamaPure-100) and ultra-high purity nitric acid prepared for the semiconductor industry, both provided by Tama Chemical Industry Co., Ltd (Tokyo, Japan) were used throughout the experiments. Dilutions were carried out on a clean bench with teflon-coated volumetric ware. We analyzed the standard reference material SRM1643c provided by the National Institute of Standards and Technology for the selected elements (17). Concentrations obtained by this method were in good agreement with the certified values for all the elements examined (17).

Besides major and trace metals, we also measured  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  concentrations in drift snow by ion chromatography (SHIMADZU HIC-6A, SHIMADZU, Japan).

## Results and Discussion

Sodium is often referred to as the marine reference element. The seasonal trend for Na shows a transient increase in early October, which is superimposed on a slowly increasing background from winter to summer (Fig. 2). Previous meteorological studies have shown that meridional long-range air transports from the surrounding oceans become prominent in September to October (20,21). Since a transient increase in wind speed was observed in the period of 5–8 October in the present study (13), the

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Na peak event can be attributed to sea salt spray transported during low pressure disturbances in the austral spring. The overall trend in concentration of the chloride ion shows a good agreement with Na ( $[Cl] = 1.71 \times [Na]$ ;  $r = 0.993$ ). Chloride versus sodium ratios for 18 samples were calculated as 1.71, which is close to the sea water value of 1.73 (22).

The Mg, K, Ca, and Sr have peaks in the spring that are significantly correlated with Na and Al (Tables 1 and 2). To examine maritime contributions to these elements, enrichment factors were calculated by applying the following equation:

$$EF_{sea} = [X/Na]_{snow} / [X/Na]_{sea}$$

where X refers to the concentrations of the elements of interest (1,2,4,23). Calculated  $EF_{sea}$  for Mg, K, Ca, and Sr are almost in unity, except during late September when they are increased 2- to 10-fold. Therefore, origins other than sea salt spray must be considered during and after the peak event for these elements. Although a concentration profile of Se has a significant correlation with Na, the contribution of the sea salt spray is almost negligible  $[Se/Na]_{sea} = 3.64 \times 10^{-9}$  (22) and  $EF_{sea}$  for Se is around  $10^2$ – $10^4$ . From the studies of the composition of volcanic smoke fumes, volcanoes could be a significant source of Se (24).

Aluminum, a crustal reference element, shows a strong peak in late September and early October (Fig. 2). The second peak of Al coincides with the Na peak. Except Na and Se, all of the elements examined have a significant correlation with Al (Tables 1–3). Crustal enrichment factors near unity are obtained for Fe, Mn, Rb, Cr, Ni, V, and all the rare earth elements before late September, suggesting that all these elements are of crustal origin. High  $EF_{crust}$  values ranging from one to four orders of magnitude are observed for Pb, Cd, Cu, and Zn as previously reported (3). The possible natural source for these heavy metals could be volcanism.

Lead concentrations for the recent Antarctic surface snow has been found to be in the range of 2–13 pg/g (1,2,4,23,25). Irrespective of possible local lead emissions from Asuka Station or snow vehicles, this is almost the same value as that of drift snow from July to late September. The subsequent lead peak may be due to volcanism or anthropogenic production transported by long-range air transport processes.

Rare earth patterns are often used as tracers of atmospheric materials on a global scale because rare earth elements are chemically

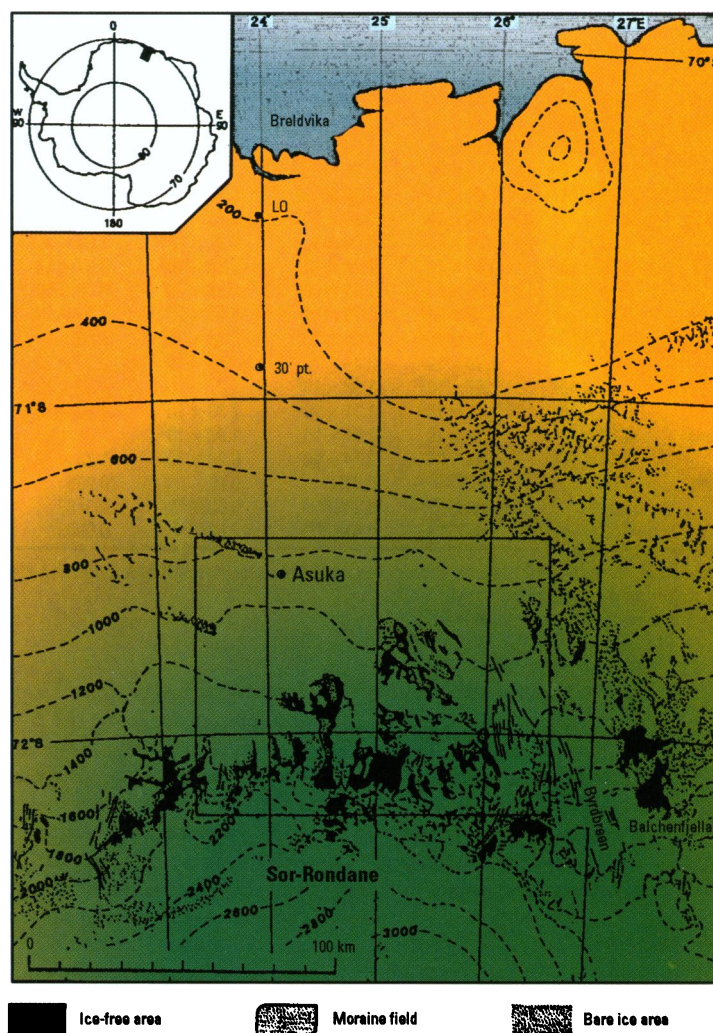


Figure 1. Asuka Station in Queen Maud Land, East Antarctica

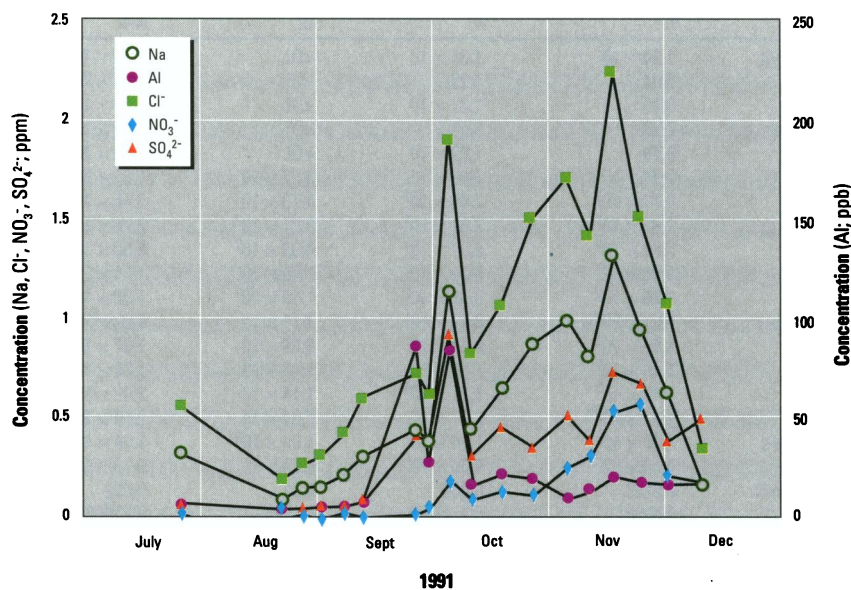


Figure 2. Seasonal concentrations of Na, Al,  $Cl^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$  in snow at Asuka Station.



**Table 1.** Seasonal variations in the concentrations of major elements

Date	Na	Mg	K	Ca	Fe	Al
25 Jul–20 Aug	$3.25 \times 10^2$	$2.58 \times 10$	$2.55 \times 10$	$1.52 \times 10$	$1.49 \times 10$	6.08
20–25 Aug	$8.90 \times 10$	9.83	9.28	7.68	$5.84 \times 10^{-1}$	4.62
25–30 Aug	$1.45 \times 10^2$	$1.78 \times 10$	$1.13 \times 10$	8.71	$7.26 \times 10^{-1}$	4.66
30 Aug–5 Sept	$1.50 \times 10^2$	$1.87 \times 10$	$1.18 \times 10$	$1.04 \times 10$	1.18	4.82
5–10 Sept	$2.11 \times 10^2$	$2.42 \times 10$	$1.58 \times 10$	$1.54 \times 10$	3.40	5.34
10–24 Sept	$3.01 \times 10^2$	$3.13 \times 10$	$2.81 \times 10$	$3.45 \times 10$	3.81	6.92
24–27 Sept	$4.38 \times 10^2$	$1.45 \times 10^2$	$1.90 \times 10^2$	$3.52 \times 10^2$	$1.63 \times 10^2$	$8.53 \times 10$
27 Sept–3 Oct	$3.73 \times 10^2$	$9.09 \times 10$	$7.89 \times 10$	$3.05 \times 10^2$	$3.53 \times 10$	$2.74 \times 10$
3–8 Oct	$1.13 \times 10^3$	$2.19 \times 10^2$	$3.94 \times 10^2$	$6.32 \times 10^2$	$1.60 \times 10^2$	$8.36 \times 10$
8–16 Oct	$4.38 \times 10^2$	$6.01 \times 10$	$7.28 \times 10$	$1.23 \times 10^2$	$3.51 \times 10$	$1.50 \times 10$
16–24 Oct	$6.50 \times 10^2$	$1.06 \times 10^2$	$7.51 \times 10$	$9.88 \times 10$	$4.35 \times 10$	$2.08 \times 10$
24 Oct–2 Nov	$8.72 \times 10^2$	$1.25 \times 10^2$	$8.72 \times 10$	$1.68 \times 10^2$	$3.51 \times 10$	$1.87 \times 10$
2–8 Nov	$9.84 \times 10^2$	$1.14 \times 10^2$	$1.06 \times 10^2$	$2.28 \times 10^2$	7.58	8.63
8–14 Nov	$7.99 \times 10^2$	$9.99 \times 10$	$8.44 \times 10$	$1.90 \times 10^2$	$1.37 \times 10$	$1.27 \times 10$
14–21 Nov	$1.30 \times 10^3$	$1.81 \times 10^2$	$1.08 \times 10^2$	$1.77 \times 10^2$	$2.23 \times 10$	$1.92 \times 10$
21–28 Nov	$9.32 \times 10^2$	$1.41 \times 10^2$	$1.01 \times 10^2$	$2.39 \times 10^2$	$2.02 \times 10$	$1.70 \times 10$
28 Nov–7 Dec	$6.16 \times 10^2$	$9.14 \times 10$	$7.91 \times 10$	$1.93 \times 10^2$	$1.84 \times 10$	$1.55 \times 10$
7–22 Dec	$1.43 \times 10^2$	$2.88 \times 10$	$2.74 \times 10$	$6.39 \times 10$	$1.75 \times 10$	$1.58 \times 10$
Detection limit	0.03	0.007	0.015	0.05	0.005	0.006
Na <sup>a</sup>	1.0000	0.8989**	0.6397**	0.6390**	0.3189	0.3383
Al <sup>a</sup>	0.3383	0.6955**	0.8747**	0.8465**	0.9909**	1.0000

Detection limits (DL) are defined here as the equivalent concentration of three times the standard deviation of the blank response (unit =  $10^{-9}$  g/g).

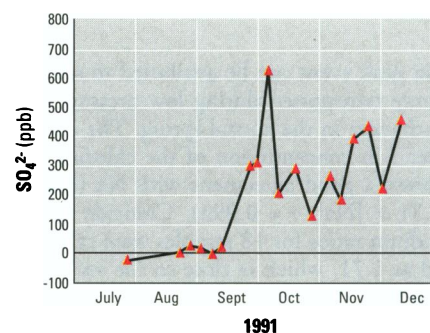
<sup>a</sup>Correlation coefficient with Na and Al by paired *t*-test.

\*\**p* < 0.01.

similar to each other and arise from the same sources (26,27). In the present study, a general trend of rare earth elements is characterized by bimodal peaks in late September and early October, as is Al (Table 3). Before peak events, the rare earth pattern in snow is similar to that in sedimentary rock; thereafter, this pattern becomes more like the rare earth pattern in acidic rock, according to Taylor's table of element abundance (28). A crustal enrichment factor for all the rare earth elements was < 5 before the peak events, and the EF<sub>crust</sub> for La, Ce, Pr, Nd, Sm, Gd, and Th

increased to 5–10 after the peak events. Local emissions from the Sør Rondane Mountains and long-range air transport processes could be the source of rare earth elements in the drift snow.

It is customary to refer to the SO<sub>4</sub><sup>2-</sup> for polar snows as non-sea salt (nss) SO<sub>4</sub><sup>2-</sup>, where nss SO<sub>4</sub><sup>2-</sup> is the non-sea salt concentration corrected for the marine contribution (29). Apparently, nss SO<sub>4</sub><sup>2-</sup> shows very low or even negative concentration until 24–27 September; thereafter, it increases as high as 150–650 ppb (Fig. 3). Previous

**Figure 3.** Seasonal concentrations of non-sea salt SO<sub>4</sub><sup>2-</sup> in snow at Asuka Station.

studies have shown that volcanogenic SO<sub>4</sub><sup>2-</sup> is the dominant component following major eruptions in Antarctica (30). Another possible source for nss SO<sub>4</sub><sup>2-</sup> is the biogenic production in the oceans. Non-sea salt sulfate, generally in the form of sulfuric acid or ammonium sulfate, is a precursor that could be from dimethylsulfide released by the biogenic activity of the marine surfaces or carbonyl sulfide, as suggested by others (31). A significant correlation of nss SO<sub>4</sub><sup>2-</sup> with Na or Cl<sup>-</sup> in this study supports this hypothesis.

From July to late September, NO<sub>3</sub><sup>-</sup> concentration stayed below 60 ppb, gradually increased to 570 ppb in mid-November, and recovered in December. Spring to early summer maximum levels in nitrate have also been confirmed in the South Pole ice cores (6–8). The sublimation process could not explain this trend very well because a maximum sublimation was thought to occur in mid- to late December, when the daily solar radiation showed its maximum (32). NO<sub>3</sub><sup>-</sup> versus nss SO<sub>4</sub><sup>2-</sup> concentration shows posi-

**Table 2.** Seasonal variations in the concentrations of trace elements

Date	Li	V	Cr	Mn	Co	Ni	Cu
25 Jul–20 Aug	$1.34 \times 10$	$1.31 \times 10$	<DL	$6.24 \times 10$	2.88	<DL	$4.16 \times 10$
20–25 Aug	7.05	7.15	<DL	$7.88 \times 10$	1.67	<DL	$3.76 \times 10$
25–30 Aug	6.15	$1.31 \times 10$	<DL	$3.15 \times 10^2$	1.21	<DL	$3.59 \times 10$
30 Aug–5 Sept	7.63	9.56	<DL	$3.83 \times 10^2$	1.98	<DL	$3.80 \times 10$
5–10 Sept	8.79	$1.20 \times 10$	<DL	$2.92 \times 10^2$	1.91	<DL	$3.94 \times 10$
10–24 Sept	$2.24 \times 10$	$2.59 \times 10$	$3.07 \times 10$	$4.81 \times 10^2$	6.86	8.17	$4.69 \times 10$
24–27 Sept	$4.02 \times 10^2$	$7.06 \times 10^2$	$4.73 \times 10^2$	$5.46 \times 10^3$	$1.64 \times 10^2$	$3.55 \times 10^2$	$2.84 \times 10^2$
27 Sept–3 Oct	$1.43 \times 10^2$	$2.51 \times 10^2$	$1.27 \times 10^2$	$3.24 \times 10^3$	$7.77 \times 10$	$1.52 \times 10^2$	$1.14 \times 10^2$
3–8 Oct	$5.92 \times 10^2$	$8.07 \times 10^2$	$4.33 \times 10^2$	$6.30 \times 10^3$	$1.70 \times 10^2$	$4.41 \times 10^2$	$2.88 \times 10^2$
8–16 Oct	$7.06 \times 10$	$8.00 \times 10$	$7.45 \times 10$	$1.21 \times 10^3$	$2.80 \times 10$	$5.95 \times 10$	$7.57 \times 10$
16–24 Oct	$1.86 \times 10^2$	$3.06 \times 10^2$	$1.19 \times 10^2$	$1.98 \times 10^3$	$3.87 \times 10$	$1.14 \times 10^2$	$1.26 \times 10^2$
24 Oct–2 Nov	$1.69 \times 10^2$	$3.42 \times 10^2$	$1.11 \times 10^2$	$2.92 \times 10^3$	$5.32 \times 10$	$1.19 \times 10^2$	$1.67 \times 10^2$
2–8 Nov	$1.53 \times 10^2$	$6.53 \times 10$	$3.59 \times 10$	$1.57 \times 10^3$	$4.49 \times 10$	$9.29 \times 10$	$6.47 \times 10$
8–14 Nov	$1.19 \times 10^2$	$7.03 \times 10$	$5.48 \times 10$	$1.36 \times 10^3$	$3.86 \times 10$	$8.96 \times 10$	$7.82 \times 10$
14–21 Nov	$1.45 \times 10^2$	$1.34 \times 10^2$	$1.14 \times 10^2$	$2.49 \times 10^3$	$6.07 \times 10$	$1.05 \times 10^2$	$1.39 \times 10^2$
21–28 Nov	$1.37 \times 10^2$	$9.91 \times 10$	$5.94 \times 10$	$2.56 \times 10^3$	$5.48 \times 10$	$9.72 \times 10$	$1.05 \times 10^2$
28 Nov–7 Dec	$1.05 \times 10^2$	$1.14 \times 10^2$	$1.04 \times 10^2$	$1.94 \times 10^3$	$5.37 \times 10$	$1.00 \times 10^2$	$9.73 \times 10$
7–22 Dec	$4.46 \times 10$	$4.60 \times 10$	$6.39 \times 10$	$8.13 \times 10^2$	$2.78 \times 10$	$4.58 \times 10$	$8.16 \times 10$
Detection limit	0.0001	0.002	0.02	0.002	0.0009	0.005	0.003
Na <sup>a</sup>	0.5831*	0.4135	0.3744	0.5799*	0.5223*	0.5148*	0.5239*
Al <sup>a</sup>	0.9378**	0.9608**	0.9929**	0.9288**	0.9614**	0.9687**	0.9514**

Detection limits (DL) are defined here as the equivalent concentration of three times the standard deviation of the blank response (unit =  $10^{-9}$  g/g).

<sup>a</sup>Correlation coefficient with Na and Al by paired *t*-test.

\**p* < 0.05; \*\**p* < 0.01.

tive correlation in the present study. Recent work indicates that nitrate can enter the troposphere through stratosphere–troposphere air exchange or through the subsidence of nitrate-laden polar stratospheric clouds. The increase of tropospheric  $\text{HNO}_3$  could be reflected in spring polar precipitation during or after October, and the intensity of this process may depend on the temperature of the polar vortex (6–8).

From the meteorological data collected at Syowa Station in 1991 (19), the lowest value of daily total ozone was observed on 30 September. This ozone loss in the lower stratosphere is believed to be a new phenomenon peculiar to the 1991 polar vortex, and its relationship to volcanic activity has been suggested by Hofmann et al. (33). The eruption of Mt. Pinatubo (15N, 120E, 13–15 June 1991) caused what is believed to be the largest aerosol perturbation to the stratosphere this century (34). In addition, in the austral spring of 1991, the Antarctic lower stratosphere was characterized by a layer of volcanic aerosols from the Cerro Hudson eruption (46S, 73W, 12–15, August 1991) (35).

Lower tropospheric ozone followed a prominent seasonal change of winter maximum and summer minimum, which is very close to results of surface ozone measurements (36–38). It has been suggested that the intrusion of stratospheric ozone into the troposphere occurs over Syowa Station throughout the year and that air with low ozone concentration is transported from subpolar or middle latitudes to Antarctica through the lower troposphere from spring to early autumn.

In summary, a bulk deposition of most of the elements and non-sea salt sulfate could be transported by a long range air transport process or polar stratospheric precipitation in austral spring at Asuka Station. Particularly, it reflects the atmospheric peculiarity of austral spring in 1991, characterized by volcanic emissions of Mt. Hudson and Mt. Pinatubo. Because only one season of drifting snow data is available in this study, it should be emphasized that this phenomenon must be confirmed by further studies and snow pit chemistry.

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Zn	Ga	Se	Rb	Sr	Cd	Pb
4.85 × 10	5.19	<DL	2.09 × 10	2.28 × 10 <sup>2</sup>	<DL	1.28 × 10
6.32 × 10	2.44	<DL	8.60	8.36	<DL	1.24 × 10
5.07 × 10	2.10	<DL	1.40 × 10	1.24 × 10 <sup>2</sup>	<DL	1.22 × 10
1.20 × 10 <sup>2</sup>	5.17	<DL	1.42 × 10	1.35 × 10 <sup>2</sup>	<DL	1.08 × 10
4.61 × 10	4.61	<DL	1.40 × 10	1.78 × 10 <sup>2</sup>	<DL	1.05 × 10
5.08 × 10	1.53 × 10	<DL	5.13 × 10	2.82 × 10 <sup>2</sup>	<DL	1.19 × 10
1.02 × 10 <sup>3</sup>	2.96 × 10 <sup>2</sup>	<DL	1.32 × 10 <sup>3</sup>	2.10 × 10 <sup>3</sup>	4.34	1.35 × 10 <sup>2</sup>
3.79 × 10 <sup>2</sup>	1.22 × 10 <sup>2</sup>	7.57 × 10	5.14 × 10 <sup>2</sup>	1.50 × 10 <sup>3</sup>	<DL	3.73 × 10
9.19 × 10 <sup>2</sup>	3.40 × 10 <sup>2</sup>	1.30 × 10 <sup>2</sup>	1.61 × 10 <sup>3</sup>	3.38 × 10 <sup>3</sup>	4.55	9.68 × 10
1.79 × 10 <sup>2</sup>	5.02 × 10	<DL	1.66 × 10 <sup>2</sup>	7.12 × 10 <sup>2</sup>	<DL	5.06
5.38 × 10 <sup>2</sup>	9.47 × 10	1.32 × 10 <sup>2</sup>	2.18 × 10 <sup>2</sup>	8.73 × 10 <sup>2</sup>	<DL	4.37 × 10
4.08 × 10 <sup>2</sup>	9.01 × 10	9.52 × 10	2.24 × 10 <sup>2</sup>	1.22 × 10 <sup>3</sup>	<DL	3.96 × 10
1.29 × 10 <sup>2</sup>	5.71 × 10	1.33 × 10 <sup>2</sup>	1.57 × 10 <sup>2</sup>	1.48 × 10 <sup>3</sup>	<DL	1.22 × 10
2.21 × 10 <sup>2</sup>	5.69 × 10	1.05 × 10 <sup>2</sup>	2.42 × 10 <sup>2</sup>	1.11 × 10 <sup>3</sup>	<DL	2.07 × 10
3.24 × 10 <sup>2</sup>	9.16 × 10	1.71 × 10 <sup>2</sup>	2.33 × 10 <sup>2</sup>	2.09 × 10 <sup>3</sup>	<DL	3.60 × 10
2.40 × 10 <sup>2</sup>	8.26 × 10	1.42 × 10 <sup>2</sup>	2.22 × 10 <sup>2</sup>	1.49 × 10 <sup>3</sup>	<DL	2.28 × 10
2.06 × 10 <sup>2</sup>	7.09 × 10	1.26 × 10 <sup>2</sup>	2.48 × 10 <sup>2</sup>	1.19 × 10 <sup>3</sup>	<DL	2.86 × 10
1.26 × 10 <sup>2</sup>	2.67 × 10	<DL	9.31 × 10	3.60 × 10 <sup>2</sup>	<DL	4.29
0.003	0.001	0.06	0.003	0.0008	0.003	0.001
0.4296	0.4895*	0.6953*	0.3866	0.7945*	0.2347	0.9275**
0.9534**	0.9799**	0.0066	0.9849**	0.8038**	0.9611**	0.6395**

**Table 3.** Seasonal variations in the concentrations of rare earth elements

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
25 Jul–20 Aug	1.53	6.75	$1.21 \times 10$	1.16	3.93	<DL	<DL	<DL
20–25 Aug	1.09	3.01	4.43	$6.68 \times 10^{-1}$	2.27	<DL	<DL	<DL
25–30 Aug	1.20	2.47	5.62	$5.51 \times 10^{-1}$	2.18	<DL	<DL	<DL
30 Aug–5 Sept	1.31	2.75	4.40	1.85	2.19	<DL	<DL	<DL
5–10 Sept	1.46	2.98	5.03	$6.94 \times 10^{-1}$	2.39	<DL	<DL	<DL
10–24 Sept	2.41	8.43	$1.67 \times 10$	2.76	6.11	<DL	<DL	<DL
24–27 Sept	$3.92 \times 10$	$2.12 \times 10^2$	$4.53 \times 10^2$	$5.08 \times 10$	$1.76 \times 10^2$	$2.42 \times 10$	3.34	$2.60 \times 10$
27 Sept–3 Oct	$1.01 \times 10$	$5.59 \times 10$	$9.98 \times 10$	$1.12 \times 10$	$4.54 \times 10$	5.99	$9.13 \times 10^{-1}$	9.23
3–8 Oct	$2.49 \times 10$	$1.25 \times 10^2$	$2.32 \times 10^2$	$2.66 \times 10$	$9.15 \times 10$	$1.41 \times 10$	2.14	$1.41 \times 10$
8–16 Oct	5.48	$2.35 \times 10$	$5.40 \times 10$	5.76	$2.15 \times 10$	2.42	<DL	3.92
16–24 Oct	$1.81 \times 10$	$8.10 \times 10$	$1.64 \times 10^2$	$1.69 \times 10$	$5.91 \times 10$	8.80	1.54	$1.34 \times 10$
24 Oct–2 Nov	$1.19 \times 10$	$5.95 \times 10$	$1.09 \times 10^2$	$1.16 \times 10$	$4.14 \times 10$	5.93	$9.30 \times 10^{-1}$	6.30
2–8 Nov	3.28	$1.57 \times 10$	$2.58 \times 10$	3.00	$1.07 \times 10$	1.00	<DL	1.23
8–14 Nov	7.02	$3.49 \times 10$	$6.20 \times 10$	8.01	$2.62 \times 10$	3.93	<DL	3.64
14–21 Nov	$1.57 \times 10$	$8.06 \times 10$	$1.48 \times 10^2$	$1.55 \times 10$	$5.11 \times 10$	8.01	1.07	8.56
21–28 Nov	$1.83 \times 10$	$9.31 \times 10$	$1.92 \times 10^2$	$1.94 \times 10$	$6.19 \times 10$	9.60	1.73	$1.03 \times 10$
28 Nov–7 Dec	9.80	$4.50 \times 10$	$9.09 \times 10$	9.19	$3.33 \times 10$	4.71	$7.45 \times 10^{-1}$	5.22
7–22 Dec	$2.49 \times 10$	$2.34 \times 10^2$	$2.28 \times 10^2$	$5.62 \times 10$	$1.80 \times 10^2$	$2.26 \times 10$	1.66	$2.02 \times 10$
Detection limit	0.0009	0.0005	0.0004	<0.0005	0.002	0.001	0.0007	0.002
Na <sup>a</sup>	0.3331	0.1685	0.2965	0.0975	0.1100	0.1911	0.3200	0.2150
Al <sup>a</sup>	0.8299**	0.6662**	0.8341**	0.6472**	0.6810**	0.7290**	0.8356**	0.7573**

Detection limits (DL) are defined here as the equivalent concentration of three times the standard deviation of the blank response (unit =  $10^{-9}$  g/g).

<sup>a</sup>Correlation coefficient with Na and Al by paired *t*-test.

\*\**p*<0.01.

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Tb	Dy	Ho	Er	Tm	Yb	Lu	Th
<DL	<DL	<DL	<DL	<DL	<DL	<DL	1.43
<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<DL	<DL	<DL	<DL	<DL	<DL	<DL	1.46
2.26	9.61	1.53	3.82	$5.44 \times 10^{-1}$	3.80	$4.25 \times 10^{-1}$	$6.21 \times 10$
$4.20 \times 10^{-1}$	2.36	$4.26 \times 10^{-1}$	<DL	<DL	<DL	$1.22 \times 10^{-1}$	$1.54 \times 10$
1.32	5.96	$9.43 \times 10^{-1}$	1.63	<DL	2.27	$3.13 \times 10^{-1}$	$5.10 \times 10$
$1.13 \times 10^{-1}$	1.29	$2.60 \times 10^{-1}$	<DL	<DL	<DL	<DL	6.74
$7.69 \times 10^{-1}$	4.07	$6.47 \times 10^{-1}$	5.30	<DL	1.28	$2.43 \times 10^{-1}$	$1.54 \times 10$
$3.93 \times 10^{-1}$	2.78	$4.84 \times 10^{-1}$	<DL	<DL	1.10	$1.60 \times 10^{-1}$	$1.33 \times 10$
<DL	<DL	<DL	<DL	<DL	<DL	<DL	3.61
$2.22 \times 10^{-1}$	1.83	$2.62 \times 10^{-1}$	<DL	<DL	<DL	<DL	6.40
$6.93 \times 10^{-1}$	3.68	$6.70 \times 10^{-1}$	<DL	<DL	1.41	$1.43 \times 10^{-1}$	$1.39 \times 10$
$8.71 \times 10^{-1}$	3.59	$6.89 \times 10^{-1}$	<DL	<DL	1.69	$1.67 \times 10^{-1}$	$1.84 \times 10$
$3.67 \times 10^{-1}$	1.97	$3.66 \times 10^{-1}$	<DL	<DL	<DL	<DL	$1.09 \times 10$
1.67	6.08	1.00	<DL	$2.35 \times 10^{-1}$	1.98	$2.56 \times 10^{-1}$	$1.04 \times 10$
<0.0005	0.001	<0.0005	0.0008	<0.0005	0.001	<0.0005	<0.0005
0.2097	0.3346	0.3338	0.1074	-0.1792	0.3201	0.2981	0.3774
0.7932**	0.8313**	0.8081**	0.5716*	0.6069**	0.8077**	0.8291**	0.9837**

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